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Description

This invention relates to a block copolymer-oil composition wherein the block copolymer is a blend of poly(styrene-ethylene-butylene-styrene) triblock copolymers, which composition may also b radiation cross-linked.

Elastomeric compositions comprising block copolymers and hydrocarbon oils wherein the copolymer constitutes up to about 30% of the composition with the hydrocarbon oil constituting from about 70% to about 98% by weight of the composition are known in the art as well as methods of preparing these compositions. Examples of such compositions and their preparation are illustrated in U.S. Patents 3,676,387 to Lindlof; 3,827,999 to Crossland; 4,176,240 to Sabia; and 4,369,284 to Chen. Various compositions within this class of elastomers have different combinations of physical properties such as hardness, ultimate elongation, temperature stability, mechanical strength, surface tackiness, memory or shape recovery properties, and others. The particular combination of properties which any particular elastomer in this class of compositions will have is not predictable from the starting materials and preparation conditions with a very high degree of certainty. Slight changes in ratios of materials, types of materials used and other factors can produce drastic changes in properties of the final composition.

Radiation cross-linking has been used to modify the physical and adhesive properties of certain copolymer-oil adhesive compositions containing from 50 to 100% copolymer and 0 to 50% extender oil. Examples of such adhesive compositions are shown in U.S. Patent 3,845,787 to Haefele et al and the modification of the properties of such adhesives by radiation curing and cross-linking is illustrated in U.S. Patent 4151057 to St. Clair et al and in "Radiation Curing of PSA's Based on Thermoplastic Rubbers" by D.J. St. Clair, Adhesives Age. March 1980, pages 30-36.

US 4369284 (Chen) discloses a gelatinous composition which contains an intimate melt blend admixture of poly (ethylene-butylene-styrene) triblock copolymer having said styrene end block to ethylene and butylene centre block ratio within the ranges of from between 31:69 to 40:60, and high levels of a plasticizing oil.

EP 146172 (Stamicarbon B.V.) discloses a process for the preparation of impact resistant thermoplastic polymer mixtures based upon a mixture of a thermoplastic polymer with a rubber; impact-resistant thermoplastic polymer mixtures made thereby; and impact-resistant polymer compositions made therefrom.

In one aspect of this invention provides a composition comprising:

2 to 30 (preferably 10-25) parts by weight of a mixture of poly(styrene-ethylene-butylene-styrene) triblock copolymers; and

70 to 98 (preferably 75-90) parts by weight of a hydrocarbon oil; and

wherein the mixture of triblock copolymers comprises:

(a) a triblock copolymer having a styrene to ethylene-butylene ratio of 14-30 styrene blocks to 70 to 86 ethylene-butylene blocks; and

(b) a triblock copolymer having a styrene to ethylene-butylene ratio of 31 to 35 styrene blocks to 65 to 69 ethylene-butylene blocks; and

wherein the ratio of copolymer (a) to copolymer (b) is from 15:85 to 85:15.

The composition may be cross-linked, and it has surprisingly been found that radiation cross-linking of styrene-diene block copolymer-oil compositions having at least 70% oil gives the composition better shape retention at high temperatures without significantly changing the other physical properties of the composition, such as cone penetration and elongation.

The triblock copolymers useful in the present invention are well known in the art as poly(styrene-ethylene-butylene-styrene) triblock copolymers and are generally referred to as SEBS triblock copolymers. These copolymers have styrene end blocks and ethylene and butylene center blocks and are characterized by the ratio of styrene blocks to the combined ethylene-butylene blocks.

It has been found that a blend of two different SEBS triblock copolymers provides oil extended elastomers according to this invention having certain desired cone penetration, elongation and tensile strength properties. The mixture or blend of SEBS triblock copolymers comprise (a) a harder or stiffer triblock copolymer having a styrene to ethylene-butylene ratio of 14 to 30 styrene blocks to 70 to 86 ethylene-butylene blocks and (b) a softer, more flexible triblock copolymer having a styrene to ethylene-butylene ratio of 31 to 35 styrene blocks to 65 to 69 ethylene-butylene blocks. Preferably copolymer (a) will have a ratio of 20 to 29 styrene blocks to 71 to 80 ethylene-butylene blocks and copolymer (b) will have a ratio of 32 to 34 styrene blocks to 66 to 68 ethylene-butylene blocks and most preferably (a) will have a ratio of 28:72 and (b) will have a ratio of 33:67. The ratio of copolymer (a) to copolymer (b) can be from about 15:85 to about 85:15 and preferably can be from about 25:75 to about 75:25 and more preferably can be from about 40:60 to about 60:40.

The hydrocarbon oils useful in the composition comprising the mixture of SEBS triblock copolymers may be any of the oils conventionally used to form elastomeric materials using 70 to 98 parts by weight of oil and 2 to 30 parts by weight copolymer. The oil may be a hydrocarbon oil such as paraffinic or naphthenic oils, synthetic oils such as polybutene or polypropene oils, and mixtures thereof. The preferred oils are mixtures of non-aromatic paraffins and naphthenic hydrocarbon oils. The oils should have a minimum boiling point higher than the softening point of the triblock copolymers. The ratio of triblock copolymer mixture to the oil will generally range from about 2 to 30 parts copolymer mixtures to 70 to 98 parts oil. In general, it is preferred to use about 5 to 25 parts triblock copolymer and most preferred for many applications to use from about 12 to about 22 parts triblock copolymer.

The SEBS triblock copolymer-oil compositions of this invention can be prepared by conventional melt blending the triblock copolymers with the oil. In order to achieve adequate mixing and for the triblock copolymers to fully melt and disperse in the oil, sufficiently high temperatures and sufficient mixing shear need to be used. The mixing at the elevated temperature should be continued until the mixture is uniform and all of the triblock copolymers is evenly dispersed or blended in the oil. After sufficient mixing, the composition is then poured into the desired molds or shapes and allowed to cool. The resulting elastomeric composition can be re-melted and again cooled without any significant change in physical properties.

The triblock copolymer-oil compositions of this invention can be made having a wide range of physical properties, such as cone penetration, ultimate elongation, and tear strength, desirable for particular end use applications. In general, compositions having a cone penetration from about 50 to about 300 (10^{-1}mm) (ASTM D217-82) and an ultimate elongation of at least 200% (ASTM D412) are particularly useful as sealing materials.

The coupling agents or prorads useful in the electron beam radiation cross-linking of the block copolymer-oil composition include the conventional multifunctional coupling agents, such as trimethyl propane trimethacrylate (TMPTM) and the triacrylate (TMPTA), 1,6-hexanedimethacrylate (HDODM) and the diacrylate (HDODA) as well as other coupling agents or prorads useful for electron beam radiation cross-linking of unsaturated rubbers. The TMPTM is preferred for use with SEBS triblock copolymer-oil compositions. Photo initiators for use with UV radiation cross-linking likewise include the conventional photo initiators used for UV radiation cross-linking of unsaturated polymers such as 2,2'-diethoxyacetophenone, benzophenone, acetophenone anthraquinone, benzaldehyde, triphenylamine, benzoinethers, and benzil.

The amount of coupling agent or prorad present in the composition to be radiation cross-linked will vary from about 0.5 to about 25% by weight base on the combined weight of the copolymer and oil. In general, it will be preferred to use about 1 to about 15% coupling agent. When UV radiation is used the photoinitiator should also be added in an amount from about 0.05% to about 5% by weight of the total composition. In general an effective amount will range from about 0.1% to about 1.0% photoinitiator.

The electron beam radiation dosage will depend on the composition, its configuration and the degree of cross-linking desired. In general, the radiation does well range from about 1 megarad to about 30 megarads and preferably will be in the range of about 2 to about 25. The amount of UV radiation will likewise depend on the degree of cross-linking desired and other relevant factors.

It will be useful to use various additives for various purposes in the triblock copolymer-oil compositions of this invention. Such additives may be stabilizers, antioxidants, flame retardants, tackifiers and the like. It is useful to use antioxidants in all the compositions of this invention and in particular it is useful to use the antioxidants in the compositions of this invention which are radiation cross-linked.

The compositions of this invention have numerous uses as elastomeric materials and in particular may be used as sealing materials as illustrated in EP-A-108518 and EP-A-191609. These publications are referred to as merely exemplary uses of the compositions of this invention which will obviously have many and varied uses depending on the properties desired in the particular device or material in which these compositions are used. The radiation cross-linked compositions find particular usefulness in applications where higher tempertures are encountered. Certain of the additives can be used to enable these compositions stable at even higher temperatures.

Example and Comparative 1

The following compositions were prepared from SEBS triblock copolymers which were (a) Shell Kraton G1650 having a styrene to ethylene-butylene ratio of 28:72 and (b) Shell Kraton G1651 having a styrene to ethylene/butylene ratio of 33:67. The oil used was a non-aromatic paraffinic/naphthenic oil available from Witco under the trademark "Kaydol". An antioxidant was employed which is a hindered phenol available from Ciba-Geigy under the trade-mark "Irganox 1010". In each case the ingredients were melt blended then poured into moulds having a diameter of about 7.6 cm (three inches) and a depth of about 1.9 cm (3/4 inch)

to form test samples of the elastomeric mat rial which w re about 1,27 cm (1/2 inch) thick. For each sample th cone penetration (ASTM D217-82), the tensil strength (ASTM D412), and the ultimate longation (ASTM D412) were determined and are shown below.

Sample #	Parts by Weight	Component	Cone Penetration ($mm10^{-1}$)	Tensile Strength $kgcm^{-2}$ (psi)	Elongation (%)
1	0 20 79 1	G1651 G1650 Kaydol Irganox 1010	59	3.3 (47)	700
2	5 15 79 1	G1651 G1650 Kaydol Irganox 1010	66	6.7 (95)	980
3	10 10 79 1	G1651 G1650 Kaydol Irganox 1010	118	7.6 (108)	1430
4	15 5 79 1	G1651 G1650 Kaydol Irganox 1010	124	8.7 (123)	1760
5	20 0 79 1	G1651 G1650 Kaydol Irganox 1010	161	10.0 (142)	1810
6	10 0 89 1	G1651 G1650 Kaydol Irganox 1010	199	4.4 (63)	1730
7	5 0 94 1	G1651 G1650 Kaydol Irganox 1010	275	1.1 (16)	1300

Example 2

In this example the composition from sample number 3 of Example 1 was prepared but also included the indicated percentages of prorad TMPTM based on the total weight of the composition. Each prepared composition was then subjected to the indicated electron beam radiation dose then subjected to tests to determine the gel content, compressive modulus (Voland-Stevens LFRA Texture Analyzer) and slump resistance at 100 °C and 150 °C. The results for each sample is shown below.

Sample	PRORAD LEVEL (%)	BEAM DOSE	GEL CONTENT (%)[1]	COMPRESSIVE MODULUS $Kgcm^{-2}$(PSI)	SLUMP RESISTANCE	
					100 °C[2]	150 °C[3]
1	0	0 MRADS	0	1.8 (26.0)	Deformed	Flowed
2	0	6 MRADS	0	1.2 (17.5)	Deformed	Flowed
3	0	12 MRADS	0	6.8 (9.9)	Deformed	Flowed
4	0	24 MRADS	0	2.4 (3.4)	Deformed	Flowed
5	2	0 MRADS	0	1.9 (27.2)	Deformed	Flowed
6	2	6 MRADS	4.0	2.0 (28.0)	No slump	No slump
7	2	12 MRADS	6.8	1.8 (17.7)	No slump	No slump
8	2	24 MRADS	8.7	———	No slump	No slump
9	5	0 MRADS	0	2.5 (35.0)	Flowed	Flowed
10	5	6 MRADS	23.7	3.2 (45.6)	No slump	No slump
11	5	12 MRADS	17.9	2.3 (33.2)	No slump	No slump
12	5	24 MRADS	14.9	1.4 (19.7)	No slump	No slump
13	10	0 MRADS	0	3.0 (43.3)	Flowed	Flowed
14	10	6 MRADS	29.5	4.9 (70.0)	No slump	No slump
15	10	12 MRADS	29.7	3.5 (50.0)	No slump	No slump
16	10	24 MRADS	27.5	2.5 (36.0)	No slump	No slump

1. 72 hours in boiling toluene.
2. 16 hours
3. 16 hours

Claims

1. A composition comprising:
   2 to 30 parts by weight of a mixture of poly(styrene-ethylene-butylene-styrene) triblock copolymers; and
   70 to 98 parts by weight of a hydrocarbon oil; and
   wherein the mixture of triblock copolymers comprises:
   (a) a triblock copolymer having a styrene to ethylene-butylene ratio of 14-30 styrene blocks to 70 to 86 ethylene-butylene blocks; and
   (b) a triblock copolymer having a styrene to ethylene-butylene ratio of 31 to 35 styrene blocks to 65 to 69 ethylene-butylene blocks; and
   wherein the ratio of copolymer (a) to copolymer (b) is from 15:85 to 85:15.

2. A composition according to claim 1, wherein the ratio of triblock copolymer (a) to triblock copolymer (b) is from 25:75 to 75:25.

3. A composition according to claim 1 or 2, wherein the ratio is from about 40:60 to about 60:40.

4. A composition according to claim 1, 2 or 3 wherein triblock copolymer (a) has a ratio of 20 to 29 styrene blocks to 71 to 80 ethylene-butylene blocks and triblock copolymer (b) has a ratio of 32 to 34 styrene blocks to 66 to 68 ethylene-butylene blocks.

5. A composition according to claim 4, wherein the triblock copolymer (a) ratio is 28:72 and the triblock copolymer (b) ratio is 33:67.

6. A composition according to any preceding claim, comprising 10 to 25 parts triblock copolymers and 75 to 90 parts hydrocarbon oil.

7. A composition according to any preceding claim, in which the hydrocarbon oil comprises a naphthenic and/or paraffinic oil.

8. A composition according to claim 7, in which the hydrocarbon oil comprises a mixture of non-aromatic

paraffins and naphthenic hydrocarbon oils.

9. A composition according to any preceding claim, that additionally comprises one or more of a stabilizer, antioxidant, flam retardant and tackifier.

Revendications

1. Composition comprenant :
2 à 30 parties en poids d'un mélange de copolymères à trois blocs poly(styrène-éthylène-butylène-styrène) ; et
70 à 98 parties en poids d'une huile hydrocarbonée ;
dans laquelle le mélange de copolymères à trois blocs comprend :
(a) un copolymère à trois blocs ayant un rapport du styrène à l'ensemble éthylène-butylène de 14-30 blocs styrène à 70 à 86 blocs éthylène-butylène ; et
(b) un copolymère à trois blocs ayant un rapport du styrène à l'ensemble éthylène-butylène de 31 à 35 blocs styrène à 65 à 69 blocs éthylène-butylène ; et
dans laquelle le rapport du copolymère (a) au copolymère (b) va de 15:85 à 85:15.

2. Composition suivant la revendication 1, dans laquelle le rapport du copolymère à trois blocs (a) au copolymère à trois blocs (b) va de 25:75 à 75:25.

3. Composition suivant la revendication 1 ou 2, dans laquelle le rapport va d'environ 40:60 à environ 60:40.

4. Composition suivant la revendication 1, 2 ou 3, dans laquelle le copolymère à trois blocs (a) possède un rapport de 20 à 29 blocs styrène à 71 à 80 blocs éthylène-butylène et le copolymère à trois blocs (b) possède un rapport de 32 à 34 blocs styrène à 66 à 68 blocs éthylène-butylène.

5. Composition suivant la revendication 4, dans laquelle le copolymère à trois blocs (a) possède un rapport de 28:72 et le copolymère à trois blocs (b) possède un rapport de 33:67.

6. Composition suivant l'une quelconque des revendications précédentes, comprenant 10 à 25 parties de copolymères à trois blocs et 75 à 90 parties d'une huile hydrocarbonée.

7. Composition suivant l'une quelconque des revendications précédentes, dans laquelle l'huile hydrocarbonée consiste en une huile naphténique et/ou paraffinique.

8. Composition suivant la revendication 7, dans laquelle l'huile hydrocarbonée consiste en un mélange de paraffines non aromatiques et d'huiles hydrocarbonées naphténiques.

9. Composition suivant l'une quelconque des revendications précédentes, qui comprend en outre un ou plusieurs composés choisis entre un stabilisant, un antioxydant, un retardateur de flamme et un agent d'adhésivité.

Patentansprüche

1. Zusammensetzung, die umfaßt:
2-30 Gewichtsteile eines Gemischs von Poly(styrol/Ethylen/Butylen/Styrol)-Triblockcopolymeren; und
70-98 Gewichtsteile eines Kohlenwasserstofföls; und
wobei das Gemisch von Triblockcopolymeren umfaßt:
(a) ein Triblockcopolymer mit einem Verhältnis von Styrol zu Ethylen/Butylen von 14-30 Styrolblöcken zu 70-86 Ethylen/Butylen-Blöcken; und
(b) ein Triblockcopolymer mit einem Verhältnis von Styrol zu Ethylen/Butylen von 31-35 Styrolblöcken zu 65-69 Ethylen/Butylen-Blöcken; und
wobei das Verhältnis von Copolymer (a) zu Copolymer (b) 15:85 bis 85:15 ist.

2. Zusammensetzung nach Anspruch 1, wobei das Verhältnis von Triblockcopolymer (a) zu Triblockcopolymer (b) 25:75 bis 75:25 ist.

3. Zusamm nsetzung nach Anspruch 1 oder 2, wobei das Verhältnis ca. 40:60 bis ca. 60:40 ist.

4. Zusammensetzung nach Anspruch 1, 2 oder 3, wobei das Triblockcopolymer (a) ein Verhältnis von 20-29 Styrolblöcken zu 71-80 Ethyl n/Butylen-Blöcken und das Triblockcopolymer (b) ein Verhältnis von 32-34 Styrolblöcken zu 66-68 Ethylen/Butylen-Blöcken hat.

5. Zusammensetzung nach Anspruch 4, wobei das Verhältnis des Triblockcopolymers (a) 28:72 und das Verhältnis des Triblockcopolymers (b) 33:67 ist.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, die 10-25 Teile Triblockcopolymere und 75-90 Teile Kohlenwasserstofföl umfaßt.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei das Kohlenwasserstofföl ein naphthenisches Öl und/oder ein Paraffinöl umfaßt.

8. Zusammensetzung nach Anspruch 7, wobei das Kohlenwasserstofföl ein Gemisch von nichtaromatischen Paraffinen und naphthenischen Kohlenwasserstoffölen umfaßt.

9. Zusammensetzung nach einem der vorhergehenden Ansprüche, die zusätzlich einen Stabilisator, ein Antioxidans, ein Flammschutzmittel oder einen Klebrigmacher oder mehrere dieser Stoffe aufweist.

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